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Adsorption and Surface-Enhanced Raman of Dyes on Silver and Gold Sols[1]

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Several negatively charged dyes were investigated for their possible adsorption on the surface of silver and gold colloidal particles. Those dyes that were found to adsorb on the particles were then checked for surface enhancement of Raman scattering. Highly efficient surface-enhanced Raman scattering (SERS) was observed from a carbocyanine dye in both sols. Excitation-dependence studies as well as adsorption studies confirm the SERS nature of the Raman spectra obtained. The dye is probably aggregated on adsorption and is probably attached through the naphthalene side moiety to the surface. Less efficient SERS was also observed for copper phthalocyanine.

Introduction

Adsorption of dyes to various surfaces has been known for many years. This phenomenon is sometimes used to determine surface areas or site areas in powders.[2,3] Several problems are encountered in the use of this method, including aggregation of the dye either in the solution or in the adsorbed state. Nevertheless, dyes such as 1,1′-diethyl-2,2′-cyanine or methylene blue give rather consistent results.[3] The study of the interactions of an adsorbed dye, in both its ground and excited states, with the energy states of the conduction band or surface plasmons of a metal is also of much interest. This aspect of adsorbed dyes was discussed by Gerischer[4] for dyes adsorbed on transparent metallic films as well as other supports. Less studied is the phenomenon of dyes adsorbed on metallic colloids in aqueous solutions. An added dimension to the interest in such systems is the observation that metallic sols may participate in water-splitting reactions.[5-7]

The observation of surface-enhanced Raman scattering (SERS) from molecules adsorbed on silver, gold, and copper electrodes[8,9] opens up a new method for studying these interactions. Furthermore, SERS has recently been observed from several substrates adsorbed on silver and gold sols.[10,11] Although the explanations of the effect are still controversial,[12] some patterns seem to emerge from the large body of research accumulated so far. Participation of lone-pair electrons[9] or complex formation between the adsorbate and the surface metal[13] was invoked as essential for SERS. In the present study we attempt to detect SERS from several dyes adsorbed on colloidal silver and gold. As is shown below, at least with carbocyanine dyes, this could easily be obtained even at submicromolar concentrations.

Experimental Section

Materials. Ag_2SO_4 (Baker Analyzed reagent), $AgNO_3$ (MCB), sodium citrate (Mallinckrodt, Analytical Reagent), poly(vinyl alcohol) denoted PVA (Polysciences, hydrolysis 99.0–99.8 mol %), $NaBH_4$ (Alfa Inorganic), $HAuCl_4$ (Strem Chemicals), and the dyes (Eastman Kodak Co., laser grade) were used as received. Water was triply distilled.

Preparation of Sols. Three different kinds of Ag sols were prepared according to the following procedures:

(a) Ag_2SO_4 (80 mg) was dissolved in ca. 200 mL of hot water and then mixed with 5 g of PVA dissolved in ca. 200 mL of hot water. The mixture was then bubbled with H_2 at near boiling temperature for 3 h. The final volume was adjusted to 500 mL.

(b) A solution of 5×10^{-3} M $AgNO_3$ (100 mL) was added portionwise to 300 mL of vigorously stirred ice–cold 2×10^{-3} M $NaBH_4$. A solution of 1% PVA (50 mL) was added during the reduction. The mixture was then boiled for ca. 1 h to decompose any excess of $NaBH_4$. The final volume was adjusted to 500 mL.

(c) $AgNO_3$ (90 mg) was dissolved in 500 mL of H_2O and brought to boiling. A solution of 1% sodium citrate (10 mL) was added. The solution was kept on boiling for ca. 1 h.

The Ag sols prepared by procedures a and b were brownish and had absorption maximum at 400 nm while that prepared by procedure c was greenish yellow and had absorption maximum at 420 nm.

The following two different Au sol preparations were used:

(a) A solution of 5×10^{-3} M $HAuCl_4$ (100 mL) was added portionwise to 300 mL of vigorously stirred ice-cold 2×10^{-3} M $NaBH_4$ solution. A solution of 1% PVA (50 mL) was added during the reduction. Following completion of the reaction, the mixture was boiled for 1 h to decompose excess of $NaBH_4$. The final volume was adjusted to 500 mL.

(b) $HAuCl_4$ (240 mg) was dissolved in 500 mL of water and the solution brought to boiling. A solution of 1% sodium citrate (50 mL) was added. Boiling was continued for ca. 1 h.

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Although Au sols prepared by procedure a were purple in color and those prepared by procedure b were wine red in color, they both had absorption maxima at approximately 530 nm. Unless otherwise stated, concentrations of Au or Ag are given in gram-atoms per liter.

Instrumentation. The absorption spectra were recorded on a Cary 14 spectrophotomer.

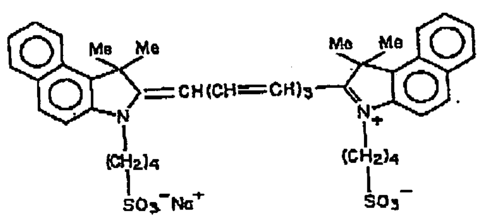
The Raman spectra were recorded on a Spex 1403 spectrometer interfaced with a Spex DPC-2 digital photometer and a Scamp system controller with data acquisition monitor processor. Coherent Radiation Ar^+ (at 514.5 nm) and Kr^+ (at 647.1 nm) lasers were used as excitation sources.

The sample cells for Raman spectra were quartz cylinders 1 cm thick and 4 cm in diameter. The scattered light was collected at 90° to the excitation beam. Spectral resolution of ± 5 cm^{-1} is estimated for the Raman signals.

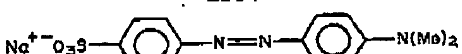
The acquisition of one Raman spectra generally took approximately 30 min. The fact that before and after taking the Raman spectrum little change was found in the absorption spectra of the dyes in water indicated that the dyes did not decompose during this period.

Results and Discussion

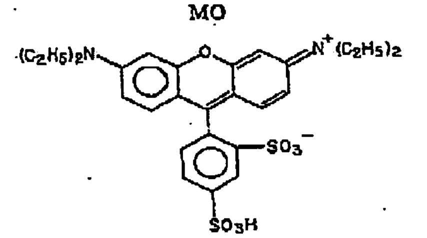
The following dyes were checked for their adsorption on silver and gold colloids: 4,5-benzoindotricarbocyanine (BICC), sulforhodamine B (SRB), copper phthalo-



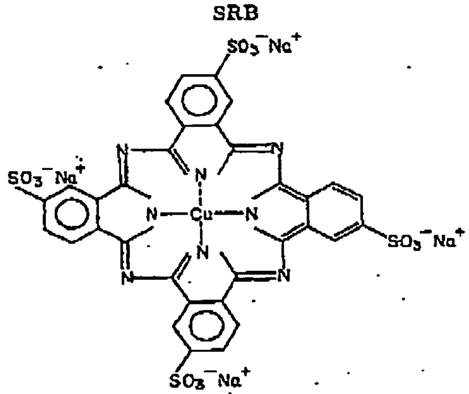
BICC



MO



SRB



CuTSPc

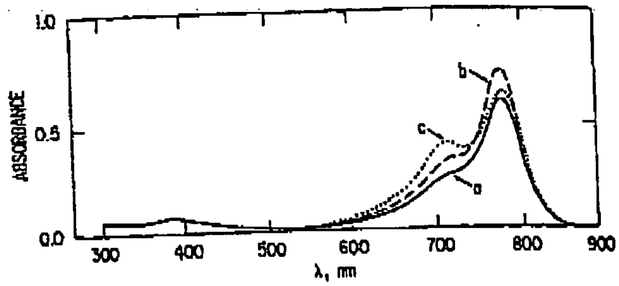


Figure 1. Absorption spectra of BICC in water. Dye concentrations: (a) 4×10^{-7} M, 10-cm cell; (b) 2.5×10^{-6} M, 2-cm cell; (c) 2×10^{-5} M 0.2-cm cell.

cyaninetetrasulfonate (CuTSPc), and methyl orange (MO). Several positively charged dyes that were checked either did not adsorb or caused coagulation of these sols and were therefore avoided. This, however, does not mean that the adsorbed dyes interact with the surface by ionic interactions. On the contrary, several results (e.g., the effect of alcohols, hydrophobicity of the dye, etc.) indicate hydrophilic interactions as the main driving force for adsorption (see below).

Aggregations and Adsorption of the Carbocynine Dye. The absorption spectra of the cyanine dye BICC at various concentrations is given in Figure 1. A major consideration in the choice of this dye for the present study was its absorption spectrum, far enough into the red and thus well separated from the sol's spectra and removed away spectrally from our lasers for the Raman excitation. Only small changes in the dye spectra could be observed when its concentration is increased from 4×10^{-7} to 2×10^{-6} M, indicating only monomeric dye molecules in this concentration range. When the dye concentration is, however, increased to 2×10^{-5} M, formation of the dimers or hypsochromic aggregates can be observed, as is apparent from the increased absorption at 700 nm relative to the monomer absorption at 778 nm.[14a] The monomer absorption peak in water is blue shifted from its position in Me_2SO[14b] ($\lambda_{max} = 795$ nm), and its absorption coefficient, $\epsilon_{778} = 1.51 \times 10^5$ M^{-1}/cm, is somewhat smaller. As can be seen in Figure 1, hardly any absorption of the dye could be detected in the spectral region where the sols absorb. In the neat aqueous solutions no formation of the bathochromic J aggregates could be observed ($\lambda_{max} = 895$ nm) at the range of concentration of up to 4×10^{-5} M. However, it was observed that the amount of the hypsochromic aggregation increases upon aging over a period of several days. All experiments were therefore performed on freshly prepared solutions. Spectra of the cyanine dye in the presence of silver sol is shown in Figure 2. The Ag sol itself absorbs light at $\lambda_{max} = 400$ nm (Figure 2a), indicating a particle radius of ~100 Å and ~2×10^5 silver atoms per particle[6] out of which ~8% are surface atoms (assuming spherical particles and 1.38-Å atomic radius for Ag). Addition of 2×10^{-5} M of BICC to the sol results only in some broadening of the sol's spectrum with hardly any absorption by dye free in the solution (Figure 2b). We could estimate that less than 10% of the dye is free in the bulk of the solution under the experimental conditions of Figure 2b. The dye could easily be recovered from the particle's surface either by addition of alcohols such as 2-propanol or 2-methyl-2-propanol (Figure 2c) or by coagulation of the sol with high concentrations of electrolytes (it was, how-

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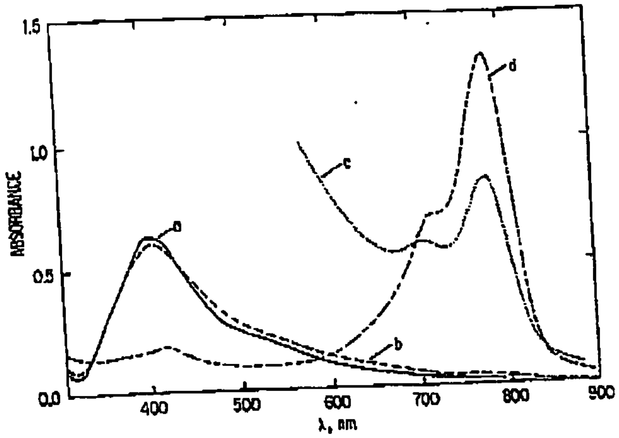

Figure 2. Absorption spectra of BICC in the presence of Ag sol: (a) 10^{-3} M PVA-stabilized silver sol only; (b) 2 × 10^{-6} M BICC in the presence of 0.9 × 10^{-3} M silver sol; (c) same as b after 1:1 dilution with 2-methyl-2-propanol; (d) same as c without Ag sol. Optical path for a and b is 0.1 cm; for ca and d, 1 cm.

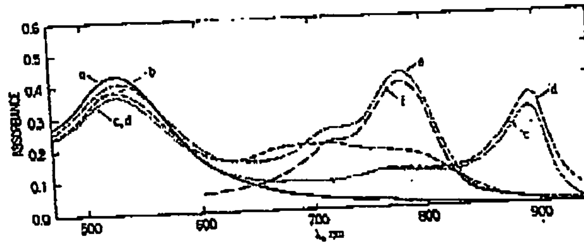

Figure 3. Absorption spectra of BICC in the presence of Au sols: (a) 1.4 × 10^{-3} M Au sol stabilized by PVA; (b) 4 × 10^{-6} M BICC in the presence of 1.1 × 10^{-3} M Au sol immediately after mixing; (c) same as b, 3 h after mixing; (d) same as b, 12 h after mixing; (e) same as c, following 1:1 dilution with 2-methyl-2-propanol; (f) same as e, without Au sol. Optical path for a–d is 0.1 cm; for e and f, 0.2 cm.

ever, noted that high concentrations (>0.1 M) of electrolytes induce aggregation of the dye even in the absence of the Ag sol). None of these effects could be observed in the presence of 0.1% PVA lone when Ag was not present in the solution. Since more than 1.5 × 10^{-6} M of the dye is adsorbed on the silver particle while, under the experimental conditions of Figure 2b, ca. 8 × 10^{-6} M of the silver atoms are at the surface, each dye molecule would require ~5 Ag atoms as an adsorption site. This leads us to conclude that either the dye molecules are stacked perpendicular to the particle surface or they aggregate in multilayers parallel to the surface. The former explanation seems more reasonable, but, either way, some degree of aggregation of the dye on adsorption has to occur.

Results similar to those described above were obtained when BICC was added to the gold sols. The absorption spectrum of the Au sol itself, peaking at 530 nm (Figure 3a), indicates the radius of the particle to be ~100 Å.[15] The number of Au atoms per particle and the percentage of Au surface atoms are therefore expected to be similar for the gold sols and the silver sols. The amount of dye adsorbed on gold was even higher than that on the silver particles. Thus 90% of 4 × 10^{-6} M BICC could be adsorbed on nominal 1.2 × 10^{-4} g-atom/L of Au sol. This would correspond to ~3 dye molecules per surface atom, which clearly indicates aggregation on the surface. At dye

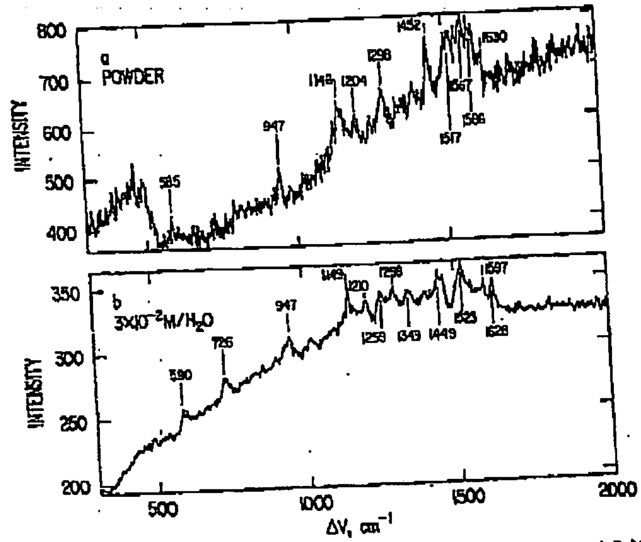

Figure 4. Raman spectra of BICC dye in powder form (a) and 3 × 10^{-2} M in H_2O (b). λ_{exc} = 514.5 nm.

concentrations ≥4 × 10^{-6} M, the behavior in the gold sols was rather different from that in silver sols. As can be seen in Figure 3, a new band centered at 895 nm slowly builds under such conditions (compare Figure 3, b, c, and d). Concomitant with the growth of the 895-nm band, one can observe a decrease in the monomer dye band at 778 nm and its aggregate band at ~700 nm. Dilution of such a sample with 2-methyl-2-propanol restores the monomer band completely (Figure 3, e and f). Dilution of a similar sample with water instead of 2-methyl-2-propanol had no effect on the shape of the spectrum, indicating that the effect of 2-methyl-2-propanol is not merely a dilution effect. We were unable to observe this band in aqueous solution in the absence of gold sol or in the silver sols. The sharpness of this band indicates that the 895-nm absorption may be assigned to J aggregates, the formation of which is clearly accelerated by the gold particles. The effect of 2-methyl-2-propanol seems to indicate that this absorption arises from aggregates adsorbed on the particle surface. Such J aggregates were previously observed on silver bromide surfaces.[16] The possibility that these are aggregates free in the solution (the formation of which will still have to be catalyzed by the gold particles probably in an adsorption–desorption process) cannot be excluded at this stage. In the latter case, addition of 2-methyl-2-propanol simply dissociates these aggregates rather than causing their desorption followed by dissociation. Since we were unable to obtain these aggregates in gold-free solutions, both possibilities should be considered at this point.

Raman Scattering of the Adsorbed Carbocyanine. The Raman spectra of the dye or, in some cases, the Raman spectra of the dye in the powder form was recorded for comparison purposes. We encountered difficulties in recording the RRS of the cyanine dye BICC, since its absorption lies at much higher wavelengths than our excitation sources. Only at high concentration (3 × 10^{-2} M) where the hypsochromic aggregates are the predominant form of this dye, could we observe signals of reasonable signal-to-noise ratio. The Raman spectrum of the powder form of BICC was also recorded, and both spectra are given

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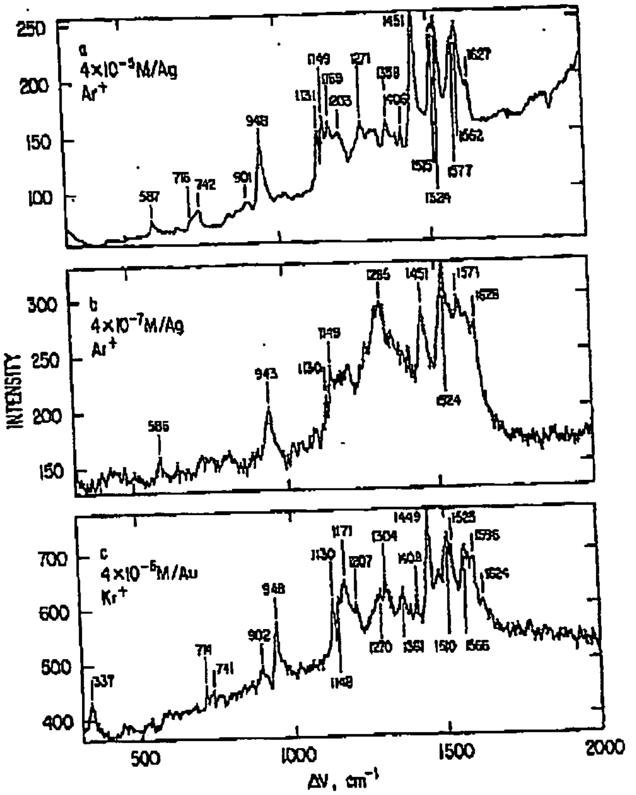

Figure 5. SERS of following: (a) 4×10^{-5} M BICC on 8×10^{-4} M Ag sol, excited at 514.5 nm; (b) as in a but 4×10^{-7} M BICC; (c) 4×10^{-5} M BICC on 1.1×10^{-3} M Au sol, excited at 647.1 nm.

in Figure 4. Although the quality of the data is rather low, many common lines could be identified in both spectra.

When the cyanine dye was added to 8×10^{-4} M of Ag/PVA sol at 4×10^{-5} M dye concentration, a sharp spectrum was easily obtained when excited with the 514.5-nm light. As mentioned above, under these conditions with the PVA-stabilized sol no light adsorption by the free dye could be observed although the dye could be recovered from the surface by addition of 2-methyl-2-propanol. The spectrum obtained under these conditions is shown in Figure 5a. The same spectrum is obtained when the Ag/PVA is prepared by using H_2, $NaBH_4$, or citrate (without PVA in the latter case) in the sol preparation procedure. Close comparison with the Raman spectrum of the dye (Figure 4) reveals common features in these spectra although, as far as could be distinguished from the low-quality powder spectrum, they are not identical. Even at every low concentrations of the dye could we observe the same spectrum. Such a spectrum, taken at 4×10^{-7} M of BICC on 0.8 mM Ag/PVA sol is shown in Figure 5b. Although the signal-to-noise ratio is lower in the later spectrum, essentially all of the lines are observed here as well.

Attempts to observe any SERS from this dye on any of the Ag sols when excited at 647.1 nm failed at either high or low concentrations of the dye. Note that although the dye, when free in solution, strongly absorbs light in this excitation region, no light is absorbed by the dye when adsorbed on the Ag particles (see Figure 2b). We estimate that the signal-to-noise ratio of the SERS under these conditions is at least 1 order of magnitude smaller than when excited with the 514.5-nm light. The opposite situation is encountered when BICC is adsorbed on the Au/PVA sols. While the dye spectrum is easily obtained when excited with the Kr^+ laser, excitation with Ar^+ laser yields at least an order of magnitude reduction in the intensity of the dye lines. The spectrum, however is identical with that obtained on Ag sols (Figure 5c) except for the line at 337 cm^{-1}, which we fail to observe on the latter sols, and the line at 587 cm^{-1}, which we observe only in the Ag adsorbed dye spectrum. These differences may arise either from different coupling of the different vibrational modes to the surface excitons upon excitation with the two different excitation sources or, less likely, from different geometrics of adsorption on the two sols.

The results described above lead us to conclude that the observed Raman spectra are due to species adsorbed on the surface. Most of the light absorption in the systems where Raman scattering could be observed is by the sols, and hardly any dye, either monomeric or aggregated was free in the solution bulk. In the absence of the sols no RRS could be obtained from the dye at such low levels of concentrations. Furthermore, the excitation characteristics are similar to those observed for pyridine adsorbed on gold and silver sols;[10,11] i.e., the excitation profile will follow the absorption spectrum of the colloid as predicted by the Mie theory rather than that of the dye. All of these lend credence to the suggestion that the Raman scattering observed is a surface-enhanced phenomenon.

Discussion of the observed Raman bands and their assignment will necessarily be deffered to a later stage. More data have to be collected and, in particular, data for similar simpler cyanine dyes are missing. Nevertheless, some assignments can be tentatively suggested. The complexity of the problem is amplified by the existence of the methyl and naphthalene side moieties in the molecule. In fact, most of the lines which were observed for the carbocyanine dye could be correlated with naphthalene bands[17] (except the 1524- and 901-cm^{-1} lines of the dye) shifted from those of the dye by less than 20 cm^{-1}. If these lines are indeed due to the naphthalene modes, this would indicate strong coupling of the naphthalene modes to surface excitations and therefore adsorption of the dye molecule through the naphthalene moiety to the surface. Other assignments, however, are obviously possible. Thus, the lines in the 1130–1200-cm^{-1} region in a series of polyenes were assigned to admixed bands of C—C stretching and C—C—H in-plane bending both coupled C═C stretching.[18] The bands at ~1500 cm^{-1} were then ascribed to C–C stretching modes. All of these bands could be correlated with many of the lines observed in the SERS of the carbocyanine dye. If such a correlation holds, then the 1524-cm^{-1} (or perhaps the 1515-cm^{-1}) line would still be above the limit of no bond alternation in the polymethine chain.[18] Although many of the lines in the dye's spectra could be correlated according to this assignment, correlation with the naphthalene vibrational spectra seems more complete.

Adsorption and SERS of Other Dyes. In Figure 6 we present the absorption spectra of CuTSPc under a variety of experimental conditions. Up to 2×10^{-6} M dye concentration, the primary species is the monomeric form with its absorption band centered at 665 nm (Figure 6a). At higher concentrations aggregation occurs with a hypsochromic shift to ~630 nm (Figure 6 b and d). Complete

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The Journal of Physical Chemistry, Vol. 86, No. 17, 1982 3395

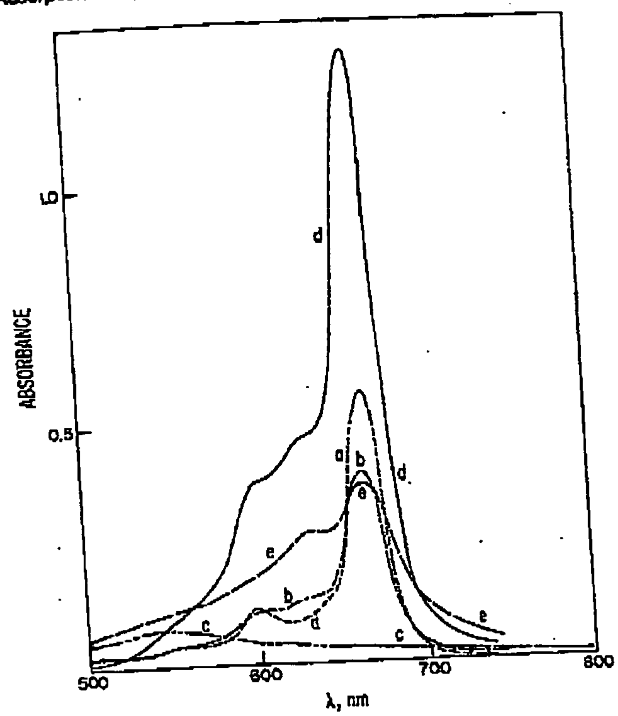

Figure 6. Absorption spectra of CuTSPc in aqueous and Au colloidal solutions. Conditions: (a) 2×10^{-5} M CuTSPc; (b) 4×10^{-5} M CuTSPc; (c) 4×10^{-5} M CuTSPc in 8×10^{-4} g-atom/L of Au sol (only Au sol spectrum is observed); (d) 8×10^{-5} M CuTSPc; (e) 8×10^{-5} M CuTSPc in 2×10^{-4} g-atom/L of Au sol. Optical path is 0.1 cm for b–e and 0.2 cm for a.

adsorption of 4×10^{-6} M of the dye to 8×10^{-4} g-atom/L of Au sol can be observed (Figure 6c). At such low [Au]/[dye] ratio complete adsorption would require aggregation on the metal surface. In Figure 6e we present the absorption spectrum of 8×10^{-5} M dye in the presence of 2×10^{-4} g-atom/L of Au sol. Even at such a high dye/Au concentration ratio, large amounts of the dye seem to adsorb on the particle's surface (compare Figure 6 e and d). The spectrum in Figure 6e, however, contains some contributions from the dye in the adsorbed state. This is indicated by the broadening of the spectrum, in particular at the red edge, compared to that of the dye in the aqueous solution. Similar broadening has been described by Gerischer for several dyes adsorbed on gold thin films.[4] Resonance Raman spectra of CuTSPC in water (4×10^{-5} M) yield lines similar to those previously observed for a number of metal phthalocyanines.[10] As indicated in the latter report, the specific central metal ion causes only minor changes in the Raman spectra, and this holds for CuTSPC as well. The lines observed upon excitation with the 647.1-nm light include the following: 1543, 1337, 1185, 956, 752, 663, and 603 cm^{-1}. When the same amount of CuTSPC was added to 1 mM of Au/PVA sol, a weak Raman spectrum was obtained when the solution was excited at 647.1 nm. We were able to identify the lines at 1581, 1438, 1347, 1202, and 691 cm^{-1} in this weak spectrum. Although these are not the same lines observed for the sol-free solution, they were observed previously in other metal phthalocyanines. It seems therefore that different vibrational modes are coupled to the excited state of the free dye and to the surface plasmon modes.

Attempts to observe SERS from the other dyes (MO and SRB) yield negative results on any of the sols with either of our two excitation sources. The absorption spectra of MO and SRB in the presence of Au sols indicate that both dyes are adsorbed on this sol as well as MO on Ag sols. Nevertheless, we fail to observe any SERS from these systems. Except for probably some experimental difficulties, we offer no explanation for this observation.

Conclusions

Adsorption of dye molecules onto colloidal Ag or Au is shown above to be a rather efficient process. Once adsorbed onto the colloidal particle, the dye may exhibit a strong surface enhancement of Raman scattering. In the case of carbocyanine dyes, this SERS could be easily observed at submicromolar dye concentrations and thus rivals in its sensitivity conventional spectrophotometry.

Very little effort was spent in the present study to assign the observed lines to particular vibrational modes. The potential of the technique is, however, rather evident. Once assignment, even in a qualitative manner, is obtained, a wealth of structural information will be available. Questions of isomerization, orientation, or degree of aggregation could then be tackled. In addition to the basic interest in understanding the interaction of dyes with the metallic surface, these questions are highly relevant to various photocatalytic processes. In view of the efficiency of silver in the SERS phenomenon, contributions from such studies to the understanding of various photographic processes are another conceivable application.